

CONTROL OF SURFACE PROPERTIES OF CHARGED POLYSULFONE/CELLULOSE ACETATE PHTHALATE FILMS WITH IMPLICATIONS IN WATER TREATMENT

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Abstract. Development of materials based on charged polysulfones were carried out as a result of their applications in membrane technology, imposing specific forms and sizes, according to the application area. Composite membranes based on quaternized polysulfones with controllable porosity and hydrophilicity degree were achieved by blending with a hydrophilic polymer, cellulose acetate phthalate. The cumulative effects of the cellulose acetate phthalate composition, charge density of polyelectrolytes, as well as the history of the formed films provide the controlling surface properties and are responsible for performance properties of the final membranes. Thus, the embedding of cellulose acetate phthalate at polysulfonic matrix improves the surface properties, surface tension parameters evaluated by contact angle measurements and also, modifies the polymer structure at morphological level, surface mechanical properties determined by specific atomic force microscopy experiments, force–distance spectroscopy DFL. The obtained results highlighted that the adhesion force values are similar to the wettability characteristics of the surface, quantified by polar component values of the surface tension, and are important in designing composites membranes used in water treatment.

Key words: quaternized polysulfone/cellulose acetate phthalate membranes, surface tension parameters, surface mechanical properties, environmental applications.

1. INTRODUCTION

During the past decade, there has been a constantly increasing of the interest on the research to improve the performance of high-polymeric membrane materials in the environment protection, drinking-water production, and medical applications [1–3]. The development of polymeric membranes with improved temperature, pH, and solvent resistance leads to use of membrane technology for solving concentration, purification, and separation problems. Regarding these issues, the use of membrane technology to treat available water resources such as brackish groundwater, seawater and the used fresh water is undeniable. Thus, the membrane processes like microfiltration, ultrafiltration, reverse osmosis, electrodialysis, used

individually or integrated appropriately with other traditional techniques have attracted much attention for the treatment of wastewater and the recovery of important products from industrial effluents [4, 5]. In this context, polysulfones (PSF) or PSF based composites have been developed and used as membrane materials in biochemical, industrial, and medical fields because of their structural and physical properties, such as the good optical properties, chemical stability, high rigidity and mechanical strength, resistance to chlorine, oxidation, and chemical compatibility resistance over wide range of pH [6, 7]. The main disadvantage of PSF membrane is due to its hydrophobic characteristics, which need to be modified for obtain high fluxes, less fouling, low maintenance cost, and widen application in different aqueous fields [8]. It is well-known that the increase of hydrophilicity of membrane will improve antifouling of the membrane. Moreover, modification of hydrophobicity of PSF membrane is helpful to reduce membrane fouling and prevent the flux-decreasing [9].

An appropriate approach to design a practical membrane material is blending with a suitable additive or the chemical modification [10, 11]. Thus, in order to improve its performance [12, 13], the PSF can be modified through chloromethylation followed by quaternization with the ammonium groups (PSFQ) of the chloromethylated polysulfones (CMPSF) [12, 14]. On the other hand, due to its simplicity, polymer blend is an attractive and efficient method with a wide diversity of properties for designing new materials. It was found that the physico-chemical characteristics of composite membranes, such as the hydrophilic/hydrophobic balance, mechanical properties, pore size, and their distribution, can be changed if the membrane is prepared from polymer blends [8]. Thereby, membranes obtained by blending hydrophobic polymers with hydrophilic polymers exhibit higher membrane fluxes and better fouling tolerance [9]. Accordingly, cellulose acetate phthalate (CAP) which has excellent characteristics [15–17], represent one of the potential hydrophilic polymers, which can be used and explored in blending with PSFQ for increase the efficiency and performance of polysulfonic membrane. Therefore, the present paper aims at exploring the performance of PSFQ/CAP composite membranes, by the control the porosity and hydrophilic properties induced by the composition of CAP hydrophilic additive, in the treatment of wastewater. The obtained results offer interesting opportunities to obtain valuable membrane materials with controlled structures and morphologies.

2. EXPERIMENTAL

2.1. MATERIALS

Polysulfone UDEL-3500 (PSF, Union Carbide Company, Texas; $M_n = 39\,000\text{ g mol}^{-1}$; $M_w/M_n = 1.625$) was purified by repeated reprecipitation from

chloroform and dried for 24 h at 40 °C, before being used in the synthesis of chloromethylated polysulfone (CMPSF) [12]. Subsequently, the ionic polysulfone containing quaternary ammonium side groups (PSFQ, $M_n = 28\,000\text{ g mol}^{-1}$) were synthesized by reacting CMPSF ($M_n = 29\,000\text{ g mol}^{-1}$ and the chlorine content of 7.42 %) with a tertiary amine, N,N-dimethylbutylamine (DMBA). The quaternization reaction was performed in N,N-dimethylformamide (DMF), as solvent, at a CMPSF/tertiary amine molar ratio of 1:1.2, for 24 h at 80 °C. The quaternary polymers were isolated from the reaction medium by precipitation in diethylether, washed 3 times with diethylether, and dried for 48 h under vacuum, at room temperature [14]. The general chemical structure of quaternized polysulfone is presented in Fig. 1.

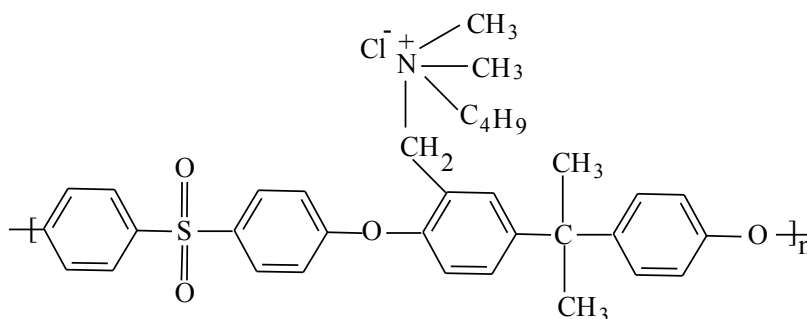


Fig. 1 – Chemical structure of quaternized polysulfone involved in the study.

The contents of ionic chlorine ($Cl_i = 5.44\%$), and total chlorine were determined by potentiometric titration (Titrator TTT1C Copenhagen), with $AgNO_3$ aqueous solutions 0.02 N. The ratio between the ionic chlorine and total chlorine contents shows that the quaternization reaction of CMPSF occurs at a transformation degree close to 98 %. Thus, one may consider that almost all chloromethylenic groups were quaternized.

Cellulose acetate phthalate (CAP), purchased from Sigma-Aldrich, USA, had a number-average molecular weight, $M_n = 2534\text{ g mol}^{-1}$ and a degree of substitution for acetyl and phthaloyl groups of 1.07 and 0.77, respectively.

2.2. FILMS PREPARATION

All films used in study were prepared by the solution-casting method. To obtain these films (around 50 μm), homogeneous casting solutions were made from PSFQ with and without CAP dissolved in N-methyl-2-pyrrolidone (NMP). Thus, the homogeneous solutions of PSFQ and CAP were prepared by dissolution in

NMP and maintained for 24 h at room temperature, followed by degassing. Different ratios, *i.e.*, 100/0, 75/25, 50/50, 25/75, and 0/100 wt./wt. of PSFQ/CAP blend were prepared by mixing the two homogeneous solutions. Subsequently, the solutions were cast on a glass plate and solidified, initially by slow drying in saturated atmosphere of the used solvent and finally, under vacuum for 2 days at 50 °C.

2.3. METHODS

2.3.1. Contact angle measurements

The static contact angles of different test liquids on surface polymer films were measured using the sessile-drop method. Uniform drops of 2 μL test liquids [double-distilled water (W), methylene iodide (CH_2I_2), and 1-brom-naphthalene (1-Bn)] were deposited on the film surface and the contact angles were measured after 30 s, with a video-based optical contact angle measuring device [18] equipped with a Hamilton syringe, in a temperature-controlled environmental chamber. The acid/base method (LW/AB) (equations 1–3) [19] was utilized for calculating the surface tension parameters of PSFQ, CAP and their blends at various ratios, *i.e.*, 75/25, 50/50, 25/75 wt./wt.

To determine the disperse and polar components of surface tension of the studied blends, knowledge on the surface tension parameters of liquids test, taken over from literature [20, 21] – Table 1, and on the values of contact angles listed in Table 2, is necessary.

$$1 + \cos \theta = \frac{2}{\gamma_{lv}} \left(\sqrt{\gamma_{sv}^{LW} \gamma_{lv}^{LW}} + \sqrt{\gamma_{sv}^+ \gamma_{lv}^-} + \sqrt{\gamma_{sv}^- \gamma_{lv}^+} \right) \quad (1)$$

$$\gamma_{sv}^{AB} = 2\sqrt{\gamma_{sv}^+ \gamma_{sv}^-}, \quad (2)$$

$$\gamma_{sv}^{LW/AB} = \gamma_{sv}^{LW} + \gamma_{sv}^{AB}, \quad (3)$$

where θ is the contact angle determined for test liquids, superscripts LW/AB, AB, and LW refer to the total surface tension, polar component (calculated from the electron-donor, γ_{sv}^- , and electron-acceptor, γ_{sv}^+ , interactions, according to equations 2), and disperse component, while subscripts “lv” and “sv” denote the liquid-vapor and surface-vapor interfacial tension.

Table 1

Surface tension parameters (mN m^{-1}) of the test liquids used for contact angle measurements

| Liquid test | γ_{lv}^d | γ_{lv}^p | γ_{lv}^+ | γ_{lv}^- | γ_{lv} |
|-------------------------|-----------------|-----------------|-----------------|-----------------|---------------|
| Water [19] | 21.80 | 51.00 | 25.50 | 25.50 | 72.80 |
| Methylene iodide [19] | 50.80 | 0 | 0.72 | 0 | 50.80 |
| 1-Brom-naphthalene [20] | 44.40 | 0 | 0 | 0 | 44.40 |

Table 2

Contact angle ($^\circ$) of different test liquids on PSFQ/CAP blend films preparation from the solutions

| Polymer/System | Contact angle | | |
|----------------|---------------|-------------------------|------|
| | W | CH_2I_2 | 1-Bn |
| PSFQ | 79 | 35 | 12 |
| CAP | 52 | 33 | 16 |
| 75/25 PSFQ/CAP | 63 | 34 | 17 |
| 50/50 PSFQ/CAP | 58 | 42 | 16 |
| 25/75 PSFQ/CAP | 55 | 33 | 10 |

2.3.2. Atomic force microscopy

Atomic force microscopy (AFM) was performed in air, at room temperature, using a Solver PRO-M Scanning Probe Microscope (NT-MDT, Zelenograd, Moscow, Russia). Due to its low resonance frequency of 87 kHz, the commercially available NSG03 rectangular-shaped silicon cantilever was used for adhesion force measurements, in contact mode. In this way, the force-distance curves measured in contact mode were obtained over the previously probed area, in tapping mode.

Force-distance spectroscopy DFL (height) was used to measure the adhesion forces between the PSFQ/CAP blends surface and silicon cantilever. In contact mode, the adhesion forces have a significant effect on the cantilever during its withdrawal from the sample. These forces cause deflection of the cantilever before it interrupts the contact with the surface. With the z-scanner length being reduced, the DFL (normal deflection distribution of the cantilever) first falls below its value, observed well away from the surface, and then abruptly reaches the free-state value, thus forming a specific dip. The adhesion force was calculated as a linear function of the probe displacement relative to the sample surface along to the Z-axis, according to Hooke's law, expressed by equation 4:

$$F_{adh} = -k\Delta x, \quad (4)$$

where k is cantilever normal spring constant of 1.97 N m^{-1} , (determined by Sader's method, using data on the resonance peak of 93 kHz and the planar dimensions of

the cantilever [22, 23]) and Δx is deflection of the cantilever in rapport with polysulfone film surface.

3. RESULTS AND DISCUSSION

Evaluation of the surface energy allows the analysis of the surface tension, according to the surface tension components generated by the synergistic effects of the polar forces, disperse (van der Waals), and hydrogen bonds (equations 1–3). In particular, the wettability and implicitly, the hydrophilicity of the studied films were determined from contact angle data. As evidenced in Table 2, which presents the results for relatively hydrophobic surfaces (with high contact angles) transformed in hydrophilic surfaces (with low contact angles) by the embedding of CAP at PSFQ matrix, the values of contact angles are affected by the polyion charge density, structural particularities of the polymers, and polymer blends composition. Thus, decrease of the contact angle is caused by the presence of polar groups of CAP, which exhibit high hydrophilicity and a corresponding increase of polymer wettability.

Polarity changes that occur on the studied polymeric films surface reflected in the results obtained for surface tension components, as well as the electron-donor and electron-acceptor parameters obtained by the LW/AB method are lists in Table 3.

Table 3

Surface tension parameters (mN m^{-1}): disperse, γ_{sv}^{LW} , and polar, γ_{sv}^{AB} , components of total surface tension, $\gamma_{sv}^{LW/AB}$, and the electron-donor, γ_{sv}^{-} , and electron-acceptor, γ_{sv}^{+} , parameters for studied composite films

| Mixing ratio (PSFQ/CAP) | γ_{sv}^{LW} | γ_{sv}^{AB} | γ_{sv}^{+} | γ_{sv}^{-} | $\gamma_{sv}^{LW/AB}$ | F_{adh} |
|-------------------------|--------------------|--------------------|-------------------|-------------------|-----------------------|------------|
| 100/0 | 43.77 | 3.91 | 10.45 | 0.37 | 47.68 | 26.35±3.01 |
| 75/25 | 43.78 | 0.13 | 24.13 | 0.002 | 43.91 | 14.59±2.44 |
| 50/50 | 42.73 | 2.73 | 18.60 | 0.100 | 45.46 | 12.92±0.79 |
| 25/75 | 42.51 | 4.47 | 20.17 | 0.250 | 46.98 | 7.47±3.15 |
| 0/100 | 42.73 | 6.42 | 23.59 | 0.44 | 49.15 | 15.30±1.20 |

As anticipated for studied systems, the values obtained for surface tension parameters indicate that apart from the nature of the functional groups spread all along the chain and charge density of the PSFQ, the history of the films formed from solutions in NMP affects these parameters. Thus, NMP being known as a typical dipolar aprotic solvent with electron-donor or hydrogen acceptor properties [24] determines conformational changes, reflected in higher viscosity of the casting solution [25] induced by the specific interactions presence in the multicomponent

system. Therefore, modification of the surface wettability characteristics represents the result of intensification of the repulsive intramolecular interactions between the ammonium groups ($\gamma_{sv,PSFQ}^+ < \gamma_{sv,CAP}^+$). It can be noted that, the addition of CAP in system leads to modifications of the local polar moments, reflected in the values of electron-donor and electron-acceptor parameters, due to the effect of chain orientation and rearrangement of the polar groups on the film surface. Additionally, PSFQ possesses the lowest hydrophilicity ($\gamma_{sv,PSFQ}^{LW} > \gamma_{sv,CAP}^{LW}$); behavior explained by intensification of the London dispersion forces, generated by fluctuations of the electron density in non-polar molecules and attractions between the instant dipoles created, and Debye dispersion forces.

On the other hand, the effect of the functional groups spread all along the polymeric chains on the surface properties, evaluated by surface free energy, ΔG_w (equation 5), evidences a high hydrophilicity of CAP and their blends, comparatively with PSFQ (Fig. 1)

$$\Delta G_w = -\gamma_{lv}(1 + \cos \theta_{water}). \quad (5)$$

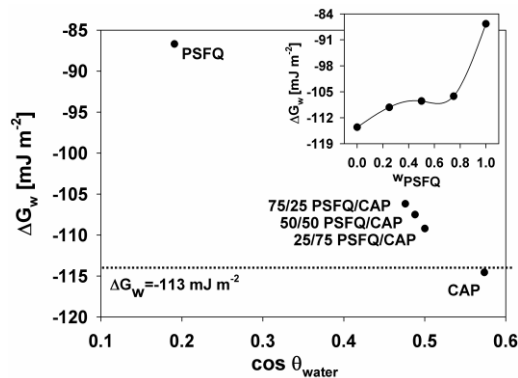


Fig. 2 – Surface free energy for films of studied PSFQ/CAP blends. The inset shows the variation of surface free energy as a function of PSFQ weight fraction.

In agreement with these remarks, the negative values of the surface free energy generally, reveals an increasing trend of wettability, and implicitly a high hydrophilicity, property necessary for application areas mentioned.

In order to design polysulfones as membrane materials, interpretation of their surface characteristics and control of their physical or/and chemical modifications should be especially had in view. In this context, the effects induced by the solvent nature and presence of CAP in polysulfonic matrix on the physical characteristics of blend were investigated at different levels, starting from the surface properties and continuing to the bulk ones. The changing trend in films

morphology, evaluated by the comparative analysis of surface state of the films among the pristine PSFQ, CAP and their blend, is in accordance with the results obtained on wettability. Thus, for pristine PSFQ the micrographs (Fig. 3a) shows the existence of irregularly shaped pores (the average diameter of the pores being of $2.16 \pm 0.28 \mu\text{m}$) disposed in some regions, in close proximity to one another, inducing a root mean square roughness (Sq) of 45.3 nm.

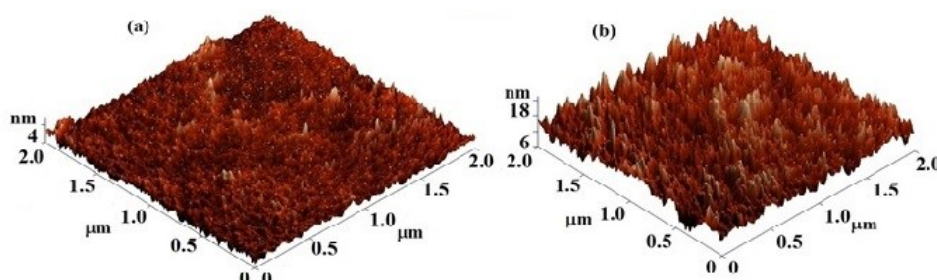


Fig. 3 – 3D AFM topography images of the pristine: (a) PSFQ; (b) CAP samples.

Instead, the pristine CAP sample presents the porous morphological formations of nanometric size ($61 \pm 22 \text{ nm}$ – Fig. 3b). By increasing of the CAP content (75/25, 50/50, 25/75 wt./wt. composition of PSFQ/CAP, Fig. 4) the morphological aspects are observable, but are not largely reflected in roughness parameters values (an increase of the Sq occurs). This behavior can be associated with a high degree of disorder in the structural distribution.

Moreover, analyzing the experimental curves of force–distance spectroscopy DFL (height) for studied blend were obtained the values of adhesion forces, F_{adh} (Table 3), which indicate the superficial wetting features in agreement with surface properties evaluated by the contact angle measurements. Thus, high value of adhesion force obtained for PSFQ in relation to lower value of adhesion force recorded for CAP, can be explained by his nature less hydrophilic ($\gamma_{sv,PSFQ}^{AB} < \gamma_{sv,CAP}^{AB}$). The values of adhesion forces obtained for PSFQ/CAP blends are similar to the wetting characteristics of the surface quantified by polar component values of the surface tension; increase the CAP content in polysulfone system, the adhesion force values decreases, indicating a more hydrophilic surface.

On the basis of above discussion, the changing trend in films morphology can be associated with the different chain conformation modifications due to the nature of solvent and also, the addition of flexible and hydrophilic groups of CAP in the casting polysulfonic solutions. Therefore, changes of the polymer blend composition in the casting solutions determines modification of pore numbers and of their characteristics, suggesting that the hydrophilicity and films porosity, which play important roles in the performance of the membrane, were enhanced.

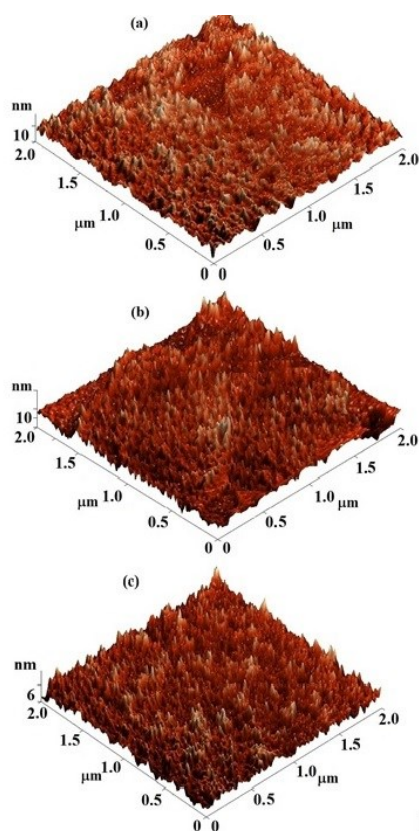


Fig. 4 – 3D AFM topography images of the PSFQ/CAP blend at different compositions: a) 75/25; b) 50/50; c) 25/75 (wt./wt.).

4. CONCLUSIONS

New quaternized polysulfones/cellulose acetate phthalate blends were investigated for establishing the structural and compositional characteristics with impact on the surface properties. The polyelectrolyte effect and hydrophilic nature of CAP in casting solution of polysulfone significantly influenced the surface tension parameters and surface free energy. Moreover, the effect of the chemical structure on the surface properties evidences a higher hydrophilicity of CAP, characterized by a surface free energy lower than -113 mJ m^{-2} . These results reflect the capacity of the N-dimethylbutylammonium chloride pendant group to determine the acceptor or donor character of the polar terms, generated by the inductive phenomena of the pendant group. Additionally, the resultant morphological structure by addition of CAP in PSFQ matrix was induced on the physical characteristics of polymers, as well as the history of the formed films. Moreover,

interactions between the hydrophobic cantilever and polymer hydrophilic substrate are reflected in values of mean adhesion force, which indicate the wettability features in agreement with surface properties evaluated by the contact angle measurements. Thus, being reported that the proper films with modeled morphology and controlled surface properties represent the better candidates to be applied in water treatment. It can be concluded that, the resulted data are important in designing composites membranes used in water treatment, where a controllable porosity and a high hydrophilicity degree are essential parameters for their reliability.

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REFERENCES

1. M. Ulbricht, *Polymer* **47**, 2217–2262 (2006).
2. M.P. Varbanets, C. Zurbrügg, C. Swartz, W. Pronk, *Water Res.* **43**, 245–265 (2009).
3. S.K. Sikdar, D. Grosse, I. Rogut, *J. Membr. Sci.* **151**, 75–85 (1998).
4. P. Le Goff, B. Benadda, C. Comel, R. Gourdon, *Sep. Sci. Technol.* **32**, 1615–1628 (1997).
5. M. Sivakumar, D.R. Mohana, R. Rangarajan, *J. Membrane Sci.* **268**, 208–219 (2006).
6. A. Rahimpour, S.S. Madaeni, *J. Membrane Sci.* **305**, 299–312 (2007).
7. M. Mulder, *Basic Principles of Membrane Technology*, Kluwer Academic Publishers, Dordrecht, 1991.
8. A. Ali, R.M. Yunus, M. Awang, M.A.C. Yunus, *Jurnal Teknologi (Sciences & Engineering)* **74**, 53–56 (2015).
9. A. Ali, R.M. Yunus, M. Awang, A. Johari, *R. Mat. Appl. Mech. Mater.* **493**, 640–644 (2014).
10. A. Higuchi, S. Mishima, T. Nakagana, *J. Membr. Sci.* **57**, 175–185 (1991).
11. A. Filimon, R.M. Albu, I. Stoica, E. Avram, *Composites Part B* **93**, 1–11 (2016).
12. E. Avram, *Polym. Plast. Technol. Eng.* **40**, 275–281 (2001).
13. A. Filimon, E. Avram, S. Dunca, *Polym. Eng. Sci.* **55**, 2184–2194 (2015).
14. C. Luca, E. Avram, I. Petrariu, *J. Macromol. Sci.: Part A – Pure Appl. Chem.* **25**, 345–361 (1988).
15. D.K. Bhat, M.S. Kumar, *Polym. Environ.* **14**, 385–392 (2006).
16. M.D. Onofrei, A.M. Dobos, S. Dunca, E.G. Ioanid, S. Ioan, *J. Appl. Polym. Sci.* **132**, 41932 (1–9) (2015).
17. A.M. Dobos, M.D. Onofrei, I. Stoica, N. Olaru, L. Olaru, S. Ioan, *Polym. Compos.* **33**, 2072–2083 (2012).
18. E.G. Ioanid, *Ro Patent* 122–166 (2008).
19. C.J. van Oss, R.J. Good, M.K. Chaudhury, *Langmuir* **4**, 884–891 (1988).
20. M. Rankl, S. Laib, S. Seeger, *Colloids Surf. B Biointer.* **30**, 177–186 (2003).
21. K. Vijayanand, K. Deepak, D.K. Pattanayak, T. R. Rama Mohan, R. Banerjee, *Trends Biomater. Artif. Organs* **18**, 73–83 (2005).
22. J.E. Sader, J.W.M. Chon, P. Mulvaney, *Rev. Sci. Instrum.* **70**, 3967–3969 (1999).
23. E. Sader, J. Pacifico, C.P. Green, P. Mulvaney, *J. Appl. Phys.* **97**, 124903–124909 (2005).
24. P.-D. Hong, H.-T. Huang, *Polymer* **41**, 6195–6204 (2000).
25. A. Filimon, A.M. Dobos, E. Avram, S. Ioan, *Pure Appl. Chem.* **86**, 1871–1882 (2014).